ENHANCEMENT OF ETHYLENE HYDROFORMYLATION OVER Ni/SiO_2 THROUGH SULFUR PROMOTION

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Sulfidation of Ni/SiO_2 with H_2S leads to a blockage of bridge-CO sites, an upward shift in the wavenumber of linearly adsorbed CO, an inhibition of ethylene hydrogenation, and an enhancement of the formation of propionaldehyde from ethylene hydroformylation.

1. Introduction

Hydroformylation is a reaction of an olefin with syngas to produce an aldehyde. The transition metals, including Rh, Ru, Co, and Pd in the form of both heterogeneous supported-metals and homogeneous metal complexes, have been shown to exhibit hydroformylation activities [1–8]. Rh and Co carbonyls and their modified forms have been employed for the commercial hydroformylation process due to their high activities and selectivities for the reaction [7,8]. Studies on the role of sulfur in homogeneous hydroformylation on the cobalt carbonyls have showed that the catalyst is highly resistant toward poisoning by sulfur compounds such as thiophene [9]. The failure of sulfur compounds to poison the hydroformylation has also been observed on the heterogeneous Rh/SiO_2 catalysts [10–11].

Recent studies have shown that Ni/SiO_2, a methanation catalyst, exhibits hydroformylation activity which is comparable to that of Rh/SiO_2 [12]. However, little is known about the effect of adsorbed sulfur on the hydroformylation over Ni/SiO_2 catalysts. In this paper, we report results of a study on ethylene hydroformylation over the sulfided Ni catalyst. In situ infrared spectroscopic (IR) method was employed to provide a better understanding of how adsorbed sulfur affects the hydroformylation reaction.

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2. Experimental

Preparation and characterization of sulfided Ni/SiO_2 has been described elsewhere [13]. Briefly, the 14.3 wt% Ni/SiO_2 was prepared by incipient wetness impregnation of SiO_2 (Strem Chemicals, No. 14-7420, SA: 350 m^2/g) with $Ni(NO_3)_2.6H_2O$ (Johnson Matthey). The Ni crystallite size was determined by X-ray diffraction-line broadening. Ethylene hydroformylation with the ratio of reactants ($CO : H_2 : C_2H_4 = 1 : 1 : 1$) was studied in an infrared (IR) cell at 240 ° C and 1–30 atm. The IR cell is made of stainless steel with CaF_2 window using Grafoil O-rings (Union Carbide). The catalysts for the study were ground to a fine powder and pressed into a disk (approx. 10 mm in diameter and 1 mm in thickness with 25 mg). Sulfidation of Ni/SiO_2 was performed by passing 1000 ppm H_2S in H_2 through the IR cell at 240 ° C and 1 atm. IR spectra of adsorbed species were recorded by a Nicolet 5SXC FTIR spectrometer with a DTGS detector at a resolution of 4 cm^{-1}. Gas phase CO bands were eliminated by subtracting the absorbance of gas phase CO with a SiO_2 disk in the cell from the spectra of adsorbed species on the Ni/SiO_2. Compositions of the effluent from the IR cell was determined by an HP-5890A gas chromatography (GC) with a 6 ft Porapak PS column in series with a 6 ft Porapak QS column.

3. Results and discussion

Table 1 shows comparison of the reaction rate and product selectivity for ethylene hydroformylation over sulfided Ni/SiO_2 (S-Ni/SiO_2) and Ni/SiO_2. The data for both catalysts were taken at the same interval since the onset of the reaction. It should be noted that the reactor was first operated in a steady-state flow mode at each specific pressure and 240 ° C for more than 30 min and the reaction pressure was increased from 1 atm to higher pressures. Our preliminary studies on the catalyst deactivation showed that the activity of both catalysts decreased with time while the product selectivity remained constant. Thus, modification of catalyst selectivity brought about by sulfur is of a major concern here.

Sulfidation led to an increase in propionaldehyde selectivity by a factor of 3–4 at 240 ° C and 1–30 atm. Such an increase in selectivity to propionaldehyde can be attributed to the reduction in the rate of ethylene hydrogenation at pressures from 1 to 30 atm and the enhancement in the rate of ethylene hydroformylation at pressures from 10 to 30 atm brought about by adsorbed sulfur. While adsorbed sulfur is known to poison olefin hydrogenation [14], it appears to be effective in promoting ethylene hydroformylation.

As the reaction pressure increased from 1 to 30 atm, the propionaldehyde selectivity increased on both catalysts. IR spectra taken for the reaction on the S-Ni/SiO_2 corresponding to the product selectivity and the rate of product

Table 1
Product distribution for ethylene hydroformylation over S-Ni/SiO_2 and Ni/SiO_2

Pressure (atm)	1		10		20		30	
Catalysts	S-Ni	Ni	S-Ni	Ni	S-Ni	Ni	S-Ni	Ni
Product selectivity (mole %)								
CH_4	4.1	2.0	0	1.3	0.2	1.1	0.2	0.6
C_{3+} H.C.	0.2	2.5	1.4	1.5	0.2	1.3	0.6	0.6
C_2H_6	83.4	92.9	66.3	87.8	64.9	89.9	58.8	87.4
Rate [a]	0.6	36.6	13.6	62.3	12.9	51.5	14.5	48.8
C_2H_5CHO	8.5	2.4	31.1	8.6	33.9	7.5	40.3	11.1
Rate [b]	0.06	0.96	6.4	6.1	6.7	4.3	9.9	6.2
C_3H_7OH	3.8	0.2	1.2	0.8	0.8	0.2	0.1	0.3

Reaction condition: 240 °C, $C_2H_4/CO/H_2 = 1:1:1$.
Total reactant flow rate = 15 cc/min.

Ni/SiO_2: Ni loading = 14.3 wt%, Ni particle size = 92 Å
S-Ni/SiO_2: the ratio of S to Ni = 0.46.

$$\text{Selectivity to a specific product (mole \%)} = \frac{\text{rate of formation of a specific product}}{\text{rate of formation for all the products}}$$

[a] the rate of C_2H_6 formation, mole/kg-hr.
[b] the rate of C_2H_5CHO formation, mole/kg-hr.

formation listed in table 1 are given in fig. 1. The major bands observed for the reaction at 1 atm are the linearly adsorbed CO at 2066 cm^{-1} and the hydrocarbon bands at 2800–3050 cm^{-1}. An increase in the reaction pressure led to (i) the growth of hydrocarbon bands and ethylene bands near 1886, 1465–1441 cm^{-1} and (ii) the shift of the peak at 2066 cm^{-1} to 2054–2057 cm^{-1} and the growth of the band at 2054 cm^{-1} corresponding to $Ni(CO)_4$ [15,16]. The absence of the linearly adsorbed CO band at high pressures appears to be due to overlapping by the strong $Ni(CO)_4$ band. $Ni(CO)_4$ was also observed in the effluent of the reactor indicating the occurrence of the transfer of $Ni(CO)_4$ from the catalyst disk to the effluent line. Chemical analysis of the catalysts (by Galbraith Lab.) show that the Ni loading decreased from 14.4% (fresh catalyst) to 6% during the entire period of the hydroformylation study.

The loss of the Ni is greater for the S-Ni/SiO_2 as compared with Ni loss for the reaction on the Ni/SiO_2 for the same reaction condition [13]. The great loss of Ni from S-Ni/SiO_2 may be due to the promoting effect of sulfur on the formation of $Ni(CO)_4$. Oudar has suggested that adsorbed sulfur could cause a weakening of the Ni substrate and the CO-substrate bond; weakly adsorbed CO

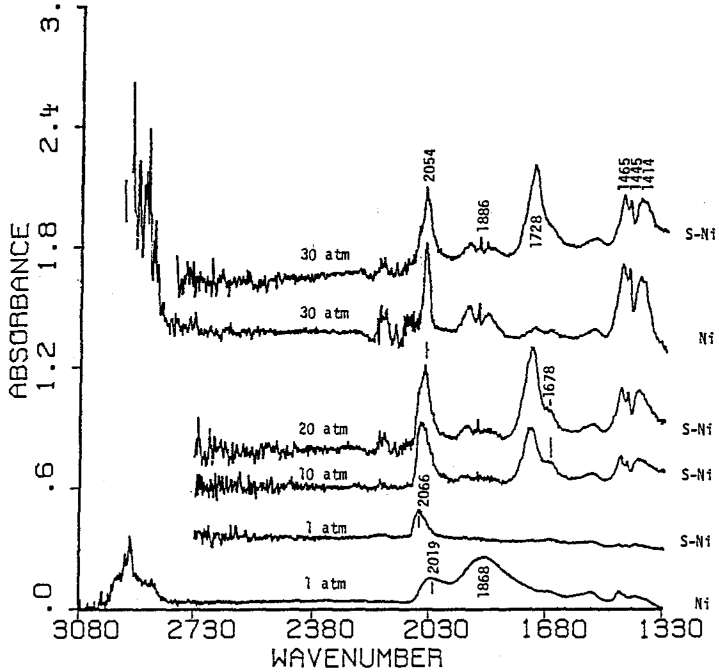

Fig. 1. Infrared spectra of ethylene hydroformylation on S-Ni/SiO_2.

would be a better candidate for the carbonyl formation than the more strongly bonded CO [14].

The adsorbed propionaldehyde band at 1728 cm^{-1} was found to increase with reaction pressures. The increase in the intensity of the band is proportional to the increase in the rate of propionaldehyde formation (table 1). The shoulder at 1678 cm^{-1} has been tentatively assigned to the vibrational frequency of an acyl species which has been suggested as the intermediate for the formation of propionaldehyde [17]. It is important to point out that the band at 1678 cm^{-1} could also be due to the C = O stretching band of some other species that are accumulating on the catalyst surface. Further study by transient technique is required to completely verify the assignment.

IR spectra of ethylene hydroformylation on the Ni/SiO_2 at 1 atm and 30 atm are shown in fig. 1. The results are consistent with our previous observations [12]. Comparison of IR spectra before and after sulfidation at 1 atm shows that sulfidation of the catalyst led to the suppression of the bridge-CO band and the shift of the linear CO to higher wavenumbers. The loss of bridge-CO sites indicates that the pair-surface Ni atoms have been disrupted by adsorbed sulfur resulting in the formation of isolated Ni atoms; the shift of the linear-CO band to higher wavenumbers may be attributed to the weakening of metal-CO bond as a result of decreases in back-donation of electron from the sulfided Ni surface to antibonding of CO molecules. However, such a shift was not obvious for the reaction at 30 atm since the prominent $Ni(CO)_4$ band may cover the weak band of absorbed CO.

Comparison of the rate and IR data at 30 atm for the S-Ni and the Ni shows that the intensity of adsorbed propionaldehyde and acyl bands and the rate of propionaldehyde formation were greater for the S-Ni/SiO_2 than for the Ni/SiO_2. The results clearly indicate that adsorbed sulfur serves as a promoter to enhance propionaldehyde formation on the Ni/SiO_2 catalyst. Although results of this study do not permit elucidation of the state of active sites for the hydroformylation on S-Ni/SiO_2, the observations of (i) lack of the bridge-CO and higher hydroformylation rate on the Ni/SiO_2 at high reaction pressures and (ii) the suppression of the bridge-CO sites and enhancement of hydroformylation brought about by adsorbed sulfur indicate that the isolated Ni-atom site may be responsible for the reaction.

Due to the ease of the formation of $Ni(CO)_4$ from sulfided Ni/SiO_2, the pure sulfided Ni catalyst is not suitable for the commercial hydroformylation. Further modification of the catalyst by addition of promoters to suppress the carbonyl formation and hydrogenation is required for the successful development of a Ni-based catalyst for commercial hydroformylation processes.

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References

[1] H.J. Gsyling, J.R. Monnier and G. Appai, J. Catal. 103 (1987) 407.
[2] P.R. Watson and G.A. Somorjai, J. Catal. 72 (1981) 347.
[3] D.S. Jordan and A.T. Bell, J. Phys. Chem. 90 (1986) 4797.
[4] O. Roelen, Ger. Pat. 849548 (1938).
[5] M. Kobayashi, Chem. Lett. (1984) 1215.
[6] S.C. Chuang, Y.H. Tian, J.G. Goodwin, Jr. and I. Wender, J. Catal. 96 (1985) 396.
[7] I. Wender and P. Pino, *Organic Synthesis via Metal Carbonyls*, Vol. 2 (John Wiley, New York, 1977).
[8] C. Masters, *Homogeneous Transition-Metal Catalysts – a Gentle Art* (Chapman and Hall, New York-London, 1981).
[9] M. Freund and L. Marko, Brennstoff-Chemie 46 (1965) 100.
[10] Y. Konishi, M. Ichikawa and W.M.H. Sachtler, J. Phys. Chem. 91 (1987) 6286.
[11] S.S.C. Chuang and S.I. Pien, J. Mol. Catal. 55 (1989) 12.
[12] S.S.C. Chuang and S.I. Pien, Catal. Lett. 3 (1989) 323.
[13] S.S.C. Chuang, S.I. Pien and C. Sze, J. Catal. (in press).
[14] J. Oudar, in: *Deactivation and Poisoning of Catalysts*, eds. J. Oudar and H. Wise (Marcel Dekker, New York, 1985) p. 51.
[15] G. Bor, Spectrochem. Acta 18 (1962) 817.
[16] D.G. Blackmond and E.I. Ko, J. Catal. 94 (1985) 343.
[17] T. Fukushima, H. Arakawa and M. Ichikawa, J. Chem. Soc., Chem. Commun. (1985) 729.